

properties of 1,2-dioxetanes and the photophysics of their cleavage products are presently in hand.

Other catalysts with acidic sites (e.g., alumina but not Norit) are also effective in catalyzing the chemiluminescent cleavage of **2**. The monoanthryl-substituted 1,2-dioxetane described earlier shows similar behavior.⁵ Since the catalyst may be removed by filtration, these heterogeneous systems offer intriguing possibilities for a practical chemiluminescent light source, which may be switched on and off. Studies of the scope and mechanism of the catalytic process are in progress.

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- (6) **1** was prepared by condensation of 2-anthraldehyde to the benzoin with KCN in aqueous ethanol followed by TsOH-catalyzed reaction of the benzoin with ethylene glycol: yellow needles; mp 285 °C; IR (KBr) 1635 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) δ 4.17 (s, 4 H, (CH₂)₂), 6.80–7.80 (m, 14 H, aromatic), 7.87 (s, 4 H, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 438 (83), 219 (9), 205 (base peak), 177 (51). Anal. Calcd for C₃₂H₂₂O₂: C, 87.64; H, 5.06. Found: C, 87.90; H, 5.10.
- (7) This sensitizer is available under the tradename SENSITOX from Hydrion Laboratories, Inc., New Brunswick, N.J. See A. P. Schaap, A. L. Thayer, E. C. Blossley, and D. C. Neckers, *J. Am. Chem. Soc.*, **97**, 3741 (1975).
- (8) The UV spectrum of **2** is similar to that of 2-methylanthracene.
- (9) The addition of singlet oxygen to **1** to yield the 1,2-dioxetane **2** as the major product contrasts with the photooxygenation of 2-(2-anthryl)-1,4-dioxene which gives both the corresponding 1,2-dioxetane and an endoperoxide.⁵ **2** will be referenced in *Chemical Abstracts* as 1,6-di(2-anthryl)-2,5,7,8-tetraoxabicyclo[4.2.0]octane.
- (10) Yellow solid; mp 253 °C; UV (*o*-xylene) λ_{max} 326 nm (log ε 3.53), 341 (3.75), 359 (3.83), 379 (3.84), 400 (3.85); IR (KBr) 1704 cm⁻¹; ¹H NMR (100 MHz, CDCl₃) δ 4.82 (s, 4 H), 6.6–9.0 (m, 18 H); mass spectrum (70 eV) *m/e* (rel intensity) 470 (1), 249 (2), 222 (2), 205 (2), 178 (7), 177 (7), 176 (4), 155 (3), 92 (10), 91 (30), 83 (base peak). Anal. Calcd for C₃₂H₂₂O₄: C, 81.68; H, 4.71. Found: C, 81.43; H, 4.65.
- (11) Determined by front face excitation. At 25 °C the fluorescence efficiency of **3** increases from 0.23 in *o*-xylene solution to a value of 0.5 in silica gel-*o*-xylene suspension (455 g/L).
- (12) The isolation procedure was hampered by the poor solubility of **3**.
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- (14) The value of the fluorescence efficiency of **3** bound to silica at 84.1 °C was taken to be identical with that at 25.0 °C.¹¹ No strong dependence of φ_F on temperature is expected. Any dependence should lead to reduced values of φ_F at higher temperatures so that the chemiluminescence efficiency may have been slightly underestimated. In *o*-xylene solution φ_F of **3** is reduced only ~25% at 84.1 °C compared to φ_F at 25.0 °C.
- (15) Relative to the radioactive light standard of Hastings: J. W. Hastings and G. Weber, *J. Opt. Soc. Am.*, **53**, 1410 (1963).
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- (20) **3** shows behavior similar to methyl 2-anthroate, e.g., UV absorption of **3** (*o*-xylene-silica gel) λ_{max} 326, 343, 361, 385, and 403 nm, with a singlet energy of 67.4 kcal/mol (compare with 70.8 kcal/mol in *o*-xylene).
- (21) Alfred P. Sloan Research Fellow, 1974–1978.

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Correlation of Chemical Shifts of Protons and Carbon-13

Sir:

We would like to draw attention to the chemical significance of a method for correlating proton and carbon-13 chemical shifts based on spin-spin coupling, information which is traditionally obtained from coherent proton decoupling over a range of different frequencies.¹⁻³ It uses a two-dimensional Fourier transform technique recently introduced by Ernst^{4,5} where one species (the *S* spins) is detected indirectly by observation of a second species (the *I* spins). A rigorous treatment of this experiment has recourse to the density matrix formalism,^{6,7} although considerable insight may be obtained by a simpler approach based on spin population arguments.⁸

The method has already been applied to the problem of correlating proton (*S*) and carbon (*I*) shifts in some simple molecules.^{8,9} The experiment consists of an initial 90° pulse applied to protons, an evolution period *t*₁ to allow free precession of the protons, a second 90° proton pulse which creates nonequilibrium spin populations, and then (simultaneously or suitably delayed) a 90° carbon-13 pulse to monitor the carbon-13 free induction decay. As the second proton pulse acts on magnetization vectors with different orientations in the transverse plane, it can be thought of as behaving in a frequency-selective manner, pumping spin populations differentially. This is how information about the proton spectrum is transmitted via the carbon-13 signal to the receiver, which is tuned to carbon-13 not protons. There is no *net* transfer of magnetization, the "new" carbon-13 resonances having positive or negative intensities with an algebraic sum of zero.^{4,5} Two-dimensional Fourier transformation generates a spectrum in two frequency dimensions containing information about protons (in the *F*₁ dimension) and carbon-13 (in the *F*₂ dimension)—essentially a shift correlation chart containing some additional information about spin coupling.

Spectra were obtained from natural-abundance carbon-13 samples on a Varian CFT-20 spectrometer provided with a program for double Fourier transformation.¹⁰ The carbon-13 free induction signals were detected under conditions of coherent off-resonance proton decoupling, causing incomplete coalescence of the proton splitting of the carbon-13 resonances in the *F*₂ dimension without allowing the antiphase components of these multiplets to come close enough together for mutual cancellation.⁸ No attempt was made to remove the corresponding doublet splitting of the proton spectra in the *F*₁ di-

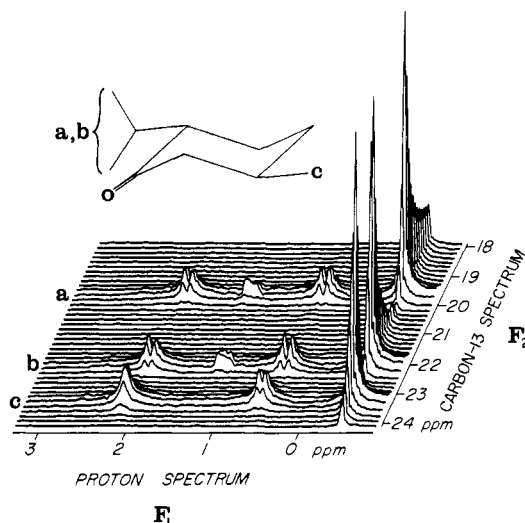


Figure 1. Two-dimensional Fourier transform spectrum (absolute value mode) of the methyl groups in menthone. The assignment of a and b remains ambiguous.

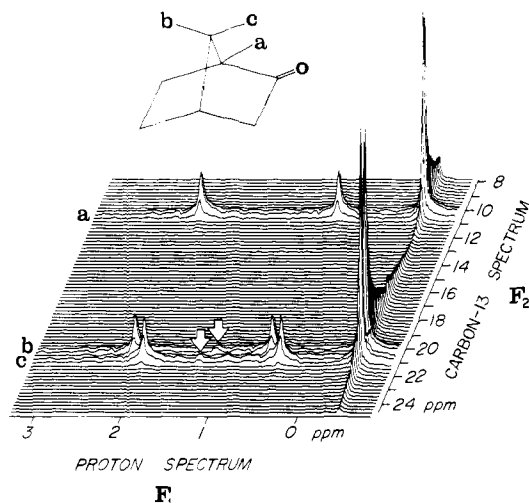


Figure 2. Two-dimensional Fourier transform spectrum (absolute value mode) of the methyl groups in camphor. Note the reversal of the proton and carbon-13 shifts of the *syn*- and *anti*-methyl groups.

mension since the CH coupling provides useful structural information. By recording the two-dimensional spectrum of tetramethylsilane, the frequency axes F_1 and F_2 have been calibrated (in parts per million) with TMS as origin. This new method of shift correlation emphasizes the importance of using a common reference material for protons and carbon-13.

We concentrate on correlating the shifts of methyl groups, since they give the clearest two-dimensional spectra, probably because of a general tendency to be only weakly coupled. Figure 1 shows the methyl region of the spectrum of menthone. Along the right-hand margin of this diagram, in the F_2 dimension, runs the spectrum of three strong decoupled lines from the unmodulated carbon-13 signals; they identify the carbon-13 shifts of sites, a, b, and c, but have no significance for correlation purposes. At each of these F_2 frequencies there is a proton spectrum running in the F_1 dimension, arising from carbon-13 signals that are modulated as a function of t_1 . Each such proton spectrum is basically a doublet due to the direct CH coupling, with proton-proton fine structure. This may well be one of the simplest ways of obtaining the proton spectrum of carbon-13 bearing molecules unencumbered by the signals from carbon-12 molecules. The mean frequency of the doublet is a good measure of the proton shift. No analysis of the proton fine structure was made, but it may be noted in spectrum c that there is an evident asymmetry attributable to strong proton-proton coupling.

Of particular interest are the responses that appear near the centres of the a and b doublets but are absent from spectrum c. These signals are transmitted through the two long-range couplings $J(C-C-CH_3)$ across the *gem*-dimethyl group. Note that the response of proton a is detected at the chemical shift of carbon b, and vice versa. This characteristic pattern may be used as a diagnostic test for geminal methyl groups, although the absence of long-range responses may only mean that the coupling is weak, leading to signal cancellation.

Figure 2 shows a section of the two-dimensional spectrum of camphor, an example of the reversal of the chemical shift effects for protons compared with carbon-13 in the c (*syn*) and b (*anti*) methyl groups. It is immediately clear that the low-field proton shift is associated with the high-field carbon-13 shift, as has been established previously by careful selective double-resonance experiments.¹¹ Weak responses transmitted through the long-range couplings in the *gem*-dimethyl group are indicated by the arrows.

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Interaction of Acetylene and Ethylene with Nickel Atom

Sir:

The interaction of π -bonded molecules such as acetylene and ethylene with zero-valent metals, particularly organometallic complexes, has long been of interest. Such species are involved in a number of important homogeneous reactions including metathesis,¹ cyclization,² hydrogenation, and dehydrogenation.³ In addition, the smaller unsaturated hydrocarbons, ethylene and acetylene in particular, have become very important in the study of heterogeneous organometallic systems. The techniques of flash desorption,⁴ UV PES,⁵ and LEED⁶ have been used extensively in an effort to elucidate the chemisorptive bonding of unsaturated molecules to metal surfaces.

To gain some detailed understanding of the electronic structure of such species, we have carried out ab initio theoretical studies of π -coordinate Ni-acetylene and Ni-ethylene complexes. The importance of such complexes as simple models for heterogeneous and homogeneous reaction systems has recently been emphasized by matrix isolation studies showing strong similarities in the properties of zero-valent monoolefin complexes and their respective chemisorbed counterparts.⁷ Accordingly, we have calculated the optimum geometry of each complex, including electron-correlation effects (generalized valence bond and configuration interaction) and characterized qualitatively the low-lying states.⁸

The results of the geometric optimization are presented in Figure 1. We find that the geometries change only slightly from those of the free molecules. In both cases the CC bond length increases by ~ 0.02 Å. For acetylene the HCC bond angle is distorted by 5° , while for ethylene the H_2C group is distorted by 2° .

The calculated Ni-C bond distances of 2.01 and 2.07 Å for acetylene and ethylene, respectively, are somewhat larger than the values for Ni-C covalent bonds (1.78 Å for $NiCH_2$ ⁹ and 1.87 Å for $NiCH_3$ ⁹) or σ lone-pair coordination bonds (1.90 Å for $NiCO$ ¹⁰). Although comparison with known organometallic complexes must be made with caution due to the other ligands present in these systems, the results appear to be consistent with the limited structural data available (e.g., $[(C_2H_4)NiP(c-C_6H_{11})_2]_2$ shows $R(CC) = 1.39$ Å and $R(NiC)$